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| (54) Title: GRANULAR AUTOMATIC DISHWASHING DETERGENT WITH LONG-CHAIN AMINE OXIDES (57) Abstract Granular automatic dishwashing detergent compositions comprising long chain amine oxides and a pH from about 6 to about 11 for enhanced greasy stain removal are disclosed. Particularly preferred compositions are substantially phosphate, silicate and boron free. | | |

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GRANULAR AUTOMATIC DISHWASHING
DETERGENT WITH LONG-CHAIN AMINE OXIDES

TECHNICAL FIELD

The present invention is in the field of automatic dishwashing detergents. More specifically, the invention relates to granular automatic dishwashing detergents and to the use in such compositions of particular amine oxides comprising one long chain and two short chains. The compositions exhibit improved removal of greasy stains, such as lipstick, and achieve cleaning on difficult substrate types, such as plastics. Also disclosed are enzyme-containing phosphate-free concentrates and a method of washing tableware, such as dishes, glassware, cups and flatware, with the compositions.

BACKGROUND OF THE INVENTION

Granular automatic dishwashing detergents (hereinafter ADDs) used for washing tableware in the home or institutionally in machines especially designed for the purpose have long been known. Dishwashing in the seventies is reviewed by Mizuno in Vol. 5, Part III of the Surfactant Science Series, Ed. W.G. Cutler and R.C. Davis, Marcel Dekker, N.Y., 1973, incorporated by reference. The particular requirements of cleansing tableware and leaving it in a sanitary, essentially spotless, residue-free state has indeed resulted in so many particular ADD compositions that the body of art pertaining thereto is now recognized as quite distinct from other cleansing product arts.

In light of legislation and current environmental trends, modern ADD products are desirably substantially free of inorganic phosphate builder salts. Unfortunately, nonphosphated ADD products in technical terms may sacrifice efficacy, especially owing to the deletion of phosphate and, in some instances, chlorine mainstay cleansing ingredients.

In addition to cleaning performance, users of ADDs have come to expect that tableware will be rendered essentially spotless and film-free. In practice, this constraint means avoiding film-forming components. The formulator must employ ingredients which are sufficiently soluble that residues or build-up do not occur in the automatic dishwashing appliance. Again, while some ingredients may be adequate on grounds of cleaning, spotting and filming, solubility considerations may diminish their usefulness. Solubility considerations are even more acute with the newer "high density", "low usage", "concentrated", ADD compositions whose overall solubility can be less than that of low-density granular products.

Yet another constraint for the formulator of ADDs is that inexpensive cleaning (for example as provided by formulations comprising high percentages by weight of sodium hydroxide or metasilicate) brings with it a severe penalty in terms of product corrosiveness. The consequences are to be found both in terms of diminished safety and in terms of damage to the dishware. It is therefore highly desirable, at least in some phosphate-free compact ADDs, to achieve good cleaning end-results without resorting to the use of high metasilicate/hydroxide formulations.

For a general review of Amine Oxides and their technological application, see Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd. Edition, Wiley, N.Y., 1978, "Amine Oxides", in Vol. 1 at pages 259-271, incorporated by reference.

Amine oxide utility in high-foaming liquid household dishwashing formulations has been disclosed: See U.S. Patents 2,999,068, 3,001,945 and Belgian 626,346. Similarly, amine oxides of various chainlength or structure can be used in laundry detergents for cleaning or antistatic action. A number of amine oxides containing one fatty chain and two methyl groups, $R^1N(O)(CH_3)_2$ wherein the fatty group R^1 is C_{12} - C_{14} have been described for use in non-automatic dishwashing detergent compositions such as liquid dishwashing detergents and shampoos. These C_{12} - C_{14} amine oxides are very high foaming; indeed, they are commonly referred to as "suds boosters". It is well known that in automatic dishwashing, the appliances, having spray-arm action,

have a low tolerance for foaming, let alone suds boosting ingredients. Even though suds suppressors, such as silicones, can resolve some degree of sudsing problems, C₁₂-C₁₄ amine oxides are relatively mass-inefficient surfactants, having critical micelle concentrations in the hundreds to thousands of parts per million. But automatic dishwashing is done with dilute products, so mass efficiency is essential. In short the C₁₂-C₁₄, or "coco" amine oxides, for a variety of reasons, are poorly suited to automatic dishwashing application.

Shorter-chain amine oxides, such as C₈ dimethylamine oxide, foam less than C₁₂-C₁₄ amine oxides but are even poorer cleaning agents, having cmc's in the thousands of ppm; thus they lack the interfacial activity to migrate from dilute solution to the interfaces of the dishes being washed by the aqueous ADD bath and cannot be used at cleaning-effective levels in granular automatic dishwashing detergents.

ADDs and their components, e.g. builders, alkaline salts, sodium silicate, low-foaming surfactants, chlorine bleach, etc., are likewise well known in the art. However, amine oxides having exactly one long chain and two short chains are not believed to have hitherto been disclosed in such compositions.

It has now unexpectedly been discovered that granular or powder-form automatic dishwashing detergents can be provided by formulating selected long-chain amine oxides having one long-chain, into ADDs having a particularly defined pH range such that the composition when dissolved at 2000-4000 ppm in an automatic dishwasher affords a pH in the range from about 6 to about 11, more preferably from about 8 to about 11, even more preferably from about 9 to about 10.5.

Preferred amine oxides in the instant ADD compositions include those having the structure $R^1(EO)_xN(O)(CH_3)_2$ wherein R¹ is a linear alkyl moiety the chainlength of which is from about 12 to about 24 carbon atoms and wherein x is from 1 to about 10; amine oxides having the structure $R^1N(O)(CH_2CH_2OH)_2$ wherein R¹ is a linear alkyl moiety the chainlength of which is from about 16 to about 18; and amine oxide dihydrates of structure

$R^1N(O)(CH_3)_2 \cdot 2H_2O$ wherein R^1 is a linear alkyl moiety the chainlength of which is from about 16 to about 18.

The novel ADDs thus afforded have the property of removing greasy film-like soils, strongly objected to by the consumer (such as lipstick stains on cups), from dishware; even when it is made of plastic. The compositions have other cleaning and spotlessness advantages; for example, for cleaning beef fat soil. ADD embodiments including phosphate free compositions and enzyme-containing compositions are provided for powerful cleaning of wide-ranging soils while retaining the advantages of a generally mild and noncorrosive product matrix.

SUMMARY OF THE INVENTION

The present invention encompasses solid-form, especially granular or powder-form automatic dishwashing detergent compositions, comprising from about 0.1% to about 10%, preferably, from about 1% to about 7%, most preferably from about 2% to about 5% of amine oxide having the general formula:

$R^1(EO)_x(PO)_y(BO)_zN(O)(CH_2R')_2 \cdot qH_2O$; (I); said compositions generally having a pH from about 6 to about 11. Preferably, the amine oxides are in solid form.

In the present invention specifically defined amine oxides permit the achieved benefits. In general formula (I), R^1 is a saturated or unsaturated hydrocarbyl moiety having a chainlength of from about 12 to about 24 carbon atoms, x is from 0 to about 10, y is from 0 to about 10, z is from 0 to about 10, R' is H or CH_2OH and q is from 0 to about 2; provided that when $x+y+z$ is 0, R^1 is saturated or unsaturated C_{16} - C_{18} ; and further provided that when $x+y+z$ is different from 0, $x+y+z$ has a maximum value of about 10.

Particularly preferred ADD embodiments contain amine oxide selected from the group consisting of hexadecyldimethylamine oxide dihydrate, octadecyldimethylamine oxide dihydrate, hexadecyl tris(ethyleneoxy)dimethylamine oxide, hexadecyldimethylamine oxide anhydrous blended with a solid-form alcohol or ethoxylated alcohol; stearyldimethylamine oxide anhydrous blended with a

solid-form alcohol or ethoxylated alcohol; and tallowbis(2-hydroxyethyl)amine oxide.

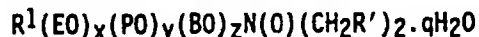
Highly preferred embodiments of the invention are substantially free from phosphate salts. Yet other preferred
5 embodiments have low (e.g., < 10% SiO₂) total silicate content. Further highly preferred embodiments are substantially boron-free.

While amine oxide and a suitable pH are the essential ingredients to the present invention, there are also provided
10 embodiments wherein additional components are desirably present. These components include but are not limited to enzymes, suds suppressors, detergent surfactants, bleaching compounds and mixtures thereof.

The present invention also encompasses a method for cleaning
15 soiled tableware comprising contacting said tableware with an aqueous medium having a pH in the range from about 6 to about 11, more preferably from about 8 to about 10, and comprising at least about 1 ppm (part per million by weight) of an amine oxide having one long-chain and two short-chains (in accordance with the above
20 formula I definition); said aqueous medium being formed by dissolving a solid-form automatic dishwashing detergent containing the essential amine oxide component in an automatic dishwashing machine.

DETAILED DESCRIPTION OF THE INVENTION

25 A solid-form automatic dishwashing detergent composition comprising from about 0.1% to about 10% by weight of an amine oxide having the general formula:

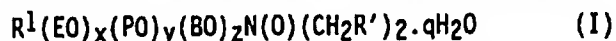


wherein R¹ represents a saturated or unsaturated hydrocarbyl
30 moiety having a chainlength of from about 12 to 24 carbon atoms, x is from 0 to about 10, y is from 0 to about 10, z is from 0 to about 10, R' is H or CH₂OH, q is from 0 to about 2, EO represents ethyleneoxy, PO represents propyleneoxy, and BO represents butyleneoxy; provided that when x+y+z = 0, R¹ has a chainlength of
35 from about 16 to about 18 carbon atoms; and further provided that when x+y+z is different from 0, x+y+z has a maximum value of 10; said composition having a pH from about 6 to about 11.

The term "substantially free" herein refers to substances that are not intentionally added to the ADD but could be present as impurities in commercial grade raw materials or feedstocks. For example, the present invention encompasses substantially phosphate-free embodiments. Such embodiments generally comprise less than 0.5% of phosphate as P₂O₅.

Amine Oxide

The ADD compositions of the present invention comprise amine oxide in accordance with the general formula I:



In general, it can be seen that the structure (I) provides one long-chain moiety $R^1(EO)_x(PO)_y(BO)_z$ and two short chain moieties, CH_2R' . R' is preferably selected from methyl and $-CH_2OH$. In general R^1 is a primary or branched hydrocarbyl moiety which can be saturated or unsaturated, preferably, R^1 is a primary alkyl moiety. When $x+y+z = 0$, R^1 is a hydrocarbyl moiety having chainlength of from about 16 to about 18. When $x+y+z$ is different from 0, R^1 may be somewhat shorter or longer, having a chainlength in the range C₁₂-C₂₄. The general formula also encompasses amine oxides wherein $x+y+z = 0$, $R^1 = C_{16}$ -C₁₈, $R' = H$ and $q = 0$ -2, preferably 2. These amine oxides are illustrated by hexadecyl dimethylamine oxide, octadecylamine oxide and their hydrates, especially the dihydrates as disclosed in U.S. Patents 5,075,501 and 5,071,594, incorporated herein by reference.

The invention also encompasses amine oxides wherein $x+y+z$ is different from zero, specifically $x+y+z$ is from about 1 to about 10, R^1 is a primary alkyl group containing 12 to about 24 carbons, preferably from about 12 to about 16 carbon atoms; in these embodiments $y + z$ is preferably 0 and x is preferably from about 1 to about 6, more preferably from about 2 to about 4; EO represents ethyleneoxy; PO represents propyleneoxy; and BO represents butyleneoxy. Such amine oxides can be prepared by conventional synthetic methods, e.g., by the reaction of alkylethoxysulfates with dimethylamine followed by oxidation of the ethoxylated amine with hydrogen peroxide.

Highly preferred amine oxides herein are solids at ambient temperature, more preferably they have melting-points in the range 30°C to 90°C. Amine oxides suitable for use herein are made commercially by a number of suppliers, including Akzo Chemie, Ethyl Corp., and Procter & Gamble. See McCutcheon's compilation and Kirk-Othmer review article for alternate amine oxide manufacturers. Preferred commercially available amine oxides are the solid, dihydrate ADMOX 16 and ADMOX 18 from Ethyl Corp.

Preferred embodiments include hexadecyldimethylamine oxide dihydrate, octadecyldimethylamine oxide dihydrate and hexadecyltris(ethyleneoxy)dimethylamine oxide.

Whereas in certain of the preferred embodiments $R' = CH_3$, there is some latitude with respect to having R' slightly larger than H. Specifically, the invention further encompasses embodiments wherein $R' = CH_2OH$, such as hexadecylbis(2-hydroxyethyl)amine oxide, tallowbis(2-hydroxyethyl)amine oxide, stearylbis(2-hydroxyethyl)amine oxide and oleylbis(2-hydroxyethyl)amine oxide.

As noted, certain preferred embodiments of the instant ADD compositions comprise amine oxide dihydrates. Conventional processes can be used to control the water content and crystallize the amine oxide in solid dihydrate form. A new process comprises (a) conventionally making amine oxide as an aqueous solution or aqueous/organic solvent solution by reacting appropriate parent amine and aqueous hydrogen peroxide (for example, 50% H_2O_2); (b) drying the product to secure substantially anhydrous amine oxide (with or without an organic solvent being present to keep the viscosity low); (c) adding two mole equivalents of water per mole of amine oxide; and (d) recrystallizing the wet amine oxide from a suitable solvent, such as ethyl acetate.

In formulating the instant ADD compositions, the amine oxide may be added to an ADD composition as a powder. This is especially appropriate in the case of the amine oxide dihydrates, since these are nonhygroscopic solids. When it is desired to use the anhydrous form of the amine oxides, it is preferable to protect the amine oxide from moisture. It is contemplated to achieve this—by conventional means, such as by applying a

relatively nonhygroscopic coating, e.g., an anhydrous coating polymer, to amine oxide particles. Alternately, and more preferably, the anhydrous amine oxide should be melted with a conventional low-melting, low-foaming waxy nonionic surfactant which is other than an amine oxide material. Such surfactants are commonly used as "sheeting agents" in granular automatic dishwashing compositions and are illustrated more fully hereinafter (see description hereinbelow of low foaming nonionic surfactant or LFNI). A desirable process comprises heating the LFNI to just above its melting-point, then adding the amine oxide steadily to the heated LFNI, optionally (but preferably) stirring to achieve a homogeneous mixture; then, optionally (but preferably) chilling the mixture. When the LFNI has a lower melting point than the amine oxide, the amine oxide need not be completely melted at any stage. The above process illustrates a manner in which the time and extent of exposure of amine oxide to heat are minimized. Once co-melted into a suitable LFNI, the combined LFNI/amine oxide may be applied to an inorganic support, e.g., a pH-adjusting component described hereinafter). One suitable approach is to form an agglomerate comprising amine oxide, LFNI and water-soluble alkaline inorganic salt or water-soluble organic or inorganic builder. In another embodiment, the amine oxide in anhydrous form is melted with a solid-form alcohol or, preferably, an ethoxylated alcohol: this may be appropriate if more cleaning action is required and less sheeting action is desired (e.g., in geographies wherein rinse-aid use is common).

Preferred amine oxides herein are substantially free of amine and/or nitrosamine ("impurity"). Preferably, the amine oxide comprises less than about 2% free amine, more preferably about 1% or lower; and less than about 500 parts per billion, more preferably less than about 50 parts per billion by weight nitrosamine.

The present invention can contain from about 0.1% to about 10%, preferably from about 1% to about 7%, more preferably from about 1.5% to about 5% of the long chain amine oxide; levels are

generally expressed on an anhydrous basis unless otherwise specifically indicated.

pH-Adjusting Component

5 The compositions herein generally comprise a pH-adjusting component selected from water-soluble alkaline inorganic salts and water-soluble organic or inorganic builders. It has been discovered that to secure the benefits of the invention, the essential long-chain amine oxide must at least be combined with said pH-adjusting component. The pH-adjusting component is selected so that when the ADD is dissolved in water at a concentration of 2000 - 4000 ppm, the pH remains in the range from about 6 to about 11, preferably from about 8 to about 11, more preferably from about 9 to about 10.5. The pH-adjusting component in preferred nonphosphate embodiments of the invention is selected from the group consisting of

10 (i) sodium carbonate or sesquicarbonate
(ii) sodium silicate, preferably hydrous sodium silicate having $\text{SiO}_2\text{:Na}_2\text{O}$ ratio of 2:1;
(iii) sodium citrate
(iv) citric acid
(v) sodium bicarbonate
(vi) sodium borate, preferably borax
(vii) sodium hydroxide; and
(viii) mixtures of (i)-(vii).

15 Preferred embodiments are substantially free of silicate (i.e. less than 10% SiO_2) and/or boron.

Preferred ADD compositions are provided comprising the essential amine oxide in combination with sodium carbonate and 2 ratio sodium silicate.

30 Illustrative of highly preferred pH-adjusting component systems are binary mixtures of granular sodium citrate with anhydrous sodium carbonate, and three-component mixtures of granular sodium citrate trihydrate, citric acid monohydrate and anhydrous sodium bicarbonate.

35 The amount of the pH adjusting component in the instant ADD compositions is generally from about 0.9% to about 99%, preferably from about 1% to about 50%, by weight of the composition. In a

preferred embodiment, the pH-adjusting component is present in the ADD composition in an amount from about 5% to about 40%, preferably from about 10% to about 30%, by weight.

5 For compositions herein having a pH between about 9.5 and about 10.5 particularly preferred ADD embodiments comprise, by weight of ADD, from about 5% to about 40%, preferably from about 10% to about 30%, most preferably from about 15% to about 20%, of sodium citrate with from about 5% to about 30%, preferably from about 7% to 25%, most preferably from about 8% to about 20% sodium carbonate.

10 Additional preferred embodiments, as more fully illustrated hereinafter, comprise pH adjusting component designed to deliver a wash pH in the range from about 8.5 to about 9.2, and are comprised of amine oxide with mixtures of citric acid, sodium citrate and sodium bicarbonate; or mixtures of amine oxide with
15 citric acid and sodium carbonate. Food-grade granular citric acid is desirably used.

The compositions of the type described herein optionally, preferably for compositions of about pH 9.5 or higher, comprise
20 alkali metal silicates. The alkali metal silicates hereinafter described provide protection against corrosion of metals and against attack on dishware, including fine china and glassware. However, sodium metasilicate is preferably avoided.

When silicates are present, the SiO_2 level should be from
25 about 1% to about 25%, preferably from about 5% to about 20%, more preferably from about 6% to about 15%, based on the weight of the ADD. The ratio of SiO_2 to the alkali metal oxide (M_2O , where M =alkali metal) is typically from about 1 to about 3.2, preferably from about 1.6 to about 3, more preferably from about 2 to about
30 2.4. Preferably, the alkali metal silicate is hydrous, having from about 15% to about 25% water, more preferably, from about 17% to about 20%.

The highly alkaline metasilicates can in general be employed, although the less alkaline hydrous alkali metal silicates having a
35 $\text{SiO}_2:\text{M}_2\text{O}$ ratio of from about 2.0 to about 2.4 are, as noted, greatly preferred. Anhydrous forms of the alkali metal silicates with a $\text{SiO}_2:\text{M}_2\text{O}$ ratio of 2.0 or more are also less preferred

because they tend to be significantly less soluble than the hydrous alkali metal silicates having the same ratio.

Sodium and potassium, and especially sodium, silicates are preferred. A particularly preferred alkali metal silicate is a granular hydrous sodium silicate having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of from 2.0 to 2.4 available from PQ Corporation, named Britesil H20 and Britesil H24. Most preferred is a granular hydrous sodium silicate having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of 2.0. While typical forms, i.e. powder and granular, of hydrous silicate particles are suitable, preferred silicate particles have a mean particle size between about 300 and about 900 microns with less than 40% smaller than 150 microns and less than 5% larger than 1700 microns. Particularly preferred is a silicate particle with a mean particle size between about 400 and about 700 microns with less than 20% smaller than 150 microns and less than 1% larger than 1700 microns. Compositions of the present invention having a pH of about 9 or less preferably will be substantially free of alkali metal silicate.

Without being bound by theory, it is believed that the pH-adjusting component is essential to prevent formation of excessive levels of the protonated form of the amine oxide component. Such protonated forms of amine oxide can undesirably deposit on dishware and limit the cleaning action of the composition. On the other hand, the pH-adjusting component is preferably selected so as to avoid excessive alkalinity, which can be corrosive to the dishware; thus, depending on the desires of the formulator, an optimum balance of greasy cleaning and material care may readily be secured.

The essential pH-adjusting system can be complemented (for improved sequestration in hard water) by other optional detergency builder salts selected from nonphosphate detergency builders known in the art, which include the various water-soluble, alkali metal, ammonium or substituted ammonium borates, hydroxysulfonates, polyacetates, and polycarboxylates. Preferred are the alkali metal, especially sodium, salts of such materials. Alternate water-soluble, non-phosphorus organic builders can be used for their sequestering properties. Examples of polyacetate and

polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediamine tetraacetic acid, ethylenediamine disuccinic acid (especially the S,S- form); nitrilotriacetic acid, tartrate monosuccinic acid, tartrate disuccinic acid, oxydisuccinic acid, carboxymethyloxysuccinic acid, mellitic acid, and sodium benzene polycarboxylate salts. Although the use of an optional detergency buider salt with strong metal-sequestering tendencies can be desirable for cleaning results, it is generally undesirable in that it may enhance corrosion of dishware.

In general, pH values of the instant compositions can vary during the course of the wash. The best procedure for determining whether a given composition has the herein-indicated pH values is as follows: make an aqueous solution or dispersion of all the ingredients of the composition by mixing them in finely divided form with the required amount of water to have a 3000 ppm total concentration. Do not have any coatings on the particles capable of inhibiting dissolution. Then measure the pH using a conventional glass electrode at ambient temperature, within about 2 minutes of forming the solution or dispersion. To be clear, this procedure relates to pH measurement and is not intended to be construed as limiting of the ADD compositions in any way; for example, it is clearly envisaged that fully-formulated embodiments of the instant ADD compositions may comprise a variety of ingredients applied as coatings to other ingredients.

Low-Foaming Nonionic Surfactant

ADD compositions of the present invention can comprise low foaming nonionic surfactants (LFNIs). LFNI can be present in amounts from 0 to about 10% by weight, preferably from about 0.25% to about 4%. LFNIs are surfactants other than amine oxides, and are most typically used in ADDs on account of the improved water-sheeting action (especially from glass) which they confer to the ADD product. They also encompass non-silicone, nonphosphate polymeric materials further illustrated hereinafter which are known to defoam food soils encountered in automatic dishwashing.

Preferred LFNIs include nonionic alkoxyated surfactants, especially ethoxylates derived from primary alcohols, and blends

thereof with more sophisticated surfactants, such as the polyoxypropylene/polyoxyethylene/polyoxypropylene reverse block polymers. The PO/EO/PO polymer-type surfactants are well-known to have foam suppressing or defoaming action, especially in relation to common food soil ingredients such as egg.

The invention encompasses preferred embodiments wherein LFNI is present, and wherein this component is solid at about 95°F (35°C), more preferably solid at about 77°F (25°C). For ease of manufacture, a preferred LFNI has a melting point between about 77°F (25°C) and about 140°F (60°C), more preferably between about 80°F (26.6°C) and 110°F (43.3°C).

In a preferred embodiment, the LFNI is an ethoxylated surfactant derived from the reaction of a monohydroxy alcohol or alkylphenol containing from about 8 to about 20 carbon atoms, excluding cyclic carbon atoms, with from about 6 to about 15 moles of ethylene oxide per mole of alcohol or alkyl phenol on an average basis.

A particularly preferred LFNI is derived from a straight chain fatty alcohol containing from about 16 to about 20 carbon atoms (C₁₆-C₂₀ alcohol), preferably a C₁₈ alcohol, condensed with an average of from about 6 to about 15 moles, preferably from about 7 to about 12 moles, and most preferably from about 7 to about 9 moles of ethylene oxide per mole of alcohol. Preferably the ethoxylated nonionic surfactant so derived has a narrow ethoxylate distribution relative to the average.

The LFNI can optionally contain propylene oxide in an amount up to about 15% by weight. Other preferred LFNI surfactants can be prepared by the processes described in U.S. Patent 4,223,163, issued September 16, 1980, Buillot, incorporated herein by reference.

Highly preferred ADDs herein wherein the LFNI is present make use of ethoxylated monohydroxy alcohol or alkyl phenol and additionally comprise a polyoxyethylene, polyoxypropylene block polymeric compound; the ethoxylated monohydroxy alcohol or alkyl phenol fraction of the LFNI comprising from about 20% to about 80%, preferably from about 30% to about 70%, of the total LFNI.

Suitable block polyoxyethylene-polyoxypropylene polymeric compounds that meet the requirements described hereinbefore include those based on ethylene glycol, propylene glycol, glycerol, trimethylolpropane and ethylenediamine as initiator
5 reactive hydrogen compound. Polymeric compounds made from a sequential ethoxylation and propoxylation of initiator compounds with a single reactive hydrogen atom, such as C₁₂₋₁₈ aliphatic alcohols, do not generally provide satisfactory suds control in the instant ADDs. Certain of the block polymer surfactant
10 compounds designated PLURONIC® and TETRONIC® by the BASF-Wyandotte Corp., Wyandotte, Michigan, are suitable in ADD compositions of the invention.

A particularly preferred LFNI contains from about 40% to about 70% of a polyoxypropylene/polyoxyethylene/polyoxypropylene
15 block polymer blend comprising about 75%, by weight of the blend, of a reverse block co-polymer of polyoxyethylene and polyoxypropylene containing 17 moles of ethylene oxide and 44 moles of propylene oxide; and about 25%, by weight of the blend, of a block co-polymer of polyoxyethylene and polyoxypropylene
20 initiated with trimethylolpropane and containing 99 moles of propylene oxide and 24 moles of ethylene oxide per mole of trimethylolpropane.

Suitable for use as LFNI in the ADD compositions are those LFNI having relatively low cloud points. Cloud points of 1%
25 solutions in water are typically below about 32°C and preferably lower, e.g., 0°C, for optimum control of sudsing throughout a full range of water temperatures.

LFNIs which may also be used include a C₁₈ alcohol polyethoxylate, having a degree of ethoxylation of about 8,
30 commercially available SLF18 from Olin Corp. and any biodegradable LFNI having the melting point properties discussed hereinabove.

Anionic Co-surfactant

The automatic dishwashing detergent compositions herein can additionally contain an anionic co-surfactant substantially free
35 of amine oxide and LFNI. When present, the anionic co-surfactant is typically in an amount from 0 to about 10%, preferably from

about 0.1% to about 8%, more preferably from about 0.5% to about 5%, by weight of the ADD composition.

Suitable anionic co-surfactants include branched or linear alkyl sulfates and sulfonates. These may contain from about 8 to about 20 carbon atoms. Other anionic cosurfactants include the alkyl benzene sulfonates containing from about 6 to about 13 carbon atoms in the alkyl group, and mono- and/or dialkyl phenyl oxide mono- and/or di-sulfonates wherein the alkyl groups contain from about 6 to about 16 carbon atoms. All of these anionic co-surfactants are used as stable salts, preferably sodium and/or potassium.

Preferred anionic co-surfactants include sulfobetaines, betaines, alkyl(polyethoxy)sulfates (AES) and alkyl (polyethoxy)carboxylates which are usually high sudsing. Optional anionic co-surfactants are further illustrated in in published British Patent Application No. 2,116,199A; U.S. Pat. No. 4,005,027, Hartman; U.S. Pat. No. 4,116,851, Rupe et al; and U.S. Pat. No. 4,116,849, Leikhim, all of which are incorporated herein by reference.

Preferred alkyl(polyethoxy)sulfate surfactants comprise a primary alkyl ethoxy sulfate derived from the condensation product of a C₆-C₁₈ alcohol with an average of from about 0.5 to about 20, preferably from about 0.5 to about 5, ethylene oxide groups. The C₆-C₁₈ alcohol itself is preferable commercially available. C₁₂-C₁₅ alkyl sulfate which has been ethoxylated with from about 1 to about 5 moles of ethylene oxide per molecule is preferred.

Where the compositions of the invention are formulated to have a pH of between 6 to 9.5, preferably between 7.5 to 9, wherein the pH is defined herein to be the pH of a 1% solution of the composition measured at 20°C, surprisingly robust soil removal, particularly proteolytic soil removal, is obtained when C₁₀-C₁₈ alkyl ethoxysulfate surfactant, with an average degree of ethoxylation of from 0.5 to 5 is incorporated into the composition in combination with a proteolytic enzyme, such as neutral or alkaline proteases at a level of active enzyme of from 0.005% to 2%. Preferred alkyl(polyethoxy)sulfate surfactants for inclusion in the present invention are the C₁₂-C₁₅ alkyl ethoxysulfate

surfactants with an average degree of ethoxylation of from 1 to 5, preferably 2 to 4, most preferably 3.

Conventional base-catalyzed ethoxylation processes to produce an average degree of ethoxylation of 12 result in a distribution of individual ethoxylates ranging from 1 to 15 ethoxy groups per mole of alcohol, so that the desired average can be obtained in a variety of ways. Blends can be made of material having different degrees of ethoxylation and/or different ethoxylate distributions arising from the specific ethoxylation techniques employed and subsequent processing steps such as distillation.

Alkyl(polyethoxy)carboxylates suitable for use herein include those with the formula $RO(CH_2CH_2O)_xCH_2COO-M^+$ wherein R is a C₆ to C₁₈ alkyl group, x ranges from 0 to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than about 20%, preferably less than about 15%, most preferably less than about 10%, and the amount of material where x is greater than 7, is less than about 25%, preferably less than about 15%, most preferably less than about 10%, the average x is from about 2 to 4 when the average R is C₁₃ or less, and the average x is from about 3 to 6 when the average R is greater than C₁₃, and M is a cation, preferably chosen from alkali metal, alkaline earth metal, ammonium, mono-, di-, and tri-ethanol-ammonium, most preferably from sodium, potassium, ammonium and mixtures thereof with magnesium ions. The preferred alkyl(polyethoxy)carboxylates are those where R is a C₁₂ to C₁₈ alkyl group.

Highly preferred anionic cosurfactants herein are sodium or potassium salt-forms for which the corresponding calcium salt form has a low Krafft temperature, e.g., 30°C or below, or, even better, 20°C or lower. Without being limited by theory, it is believed that film on hard surfaces can be minimized by using the compositions of the present invention containing calcium salts of anionic cosurfactants with low Krafft temperatures and having a pH between about 8 and about 11. Examples of such highly preferred anionic cosurfactants are the alkyl(polyethoxy)sulfates.

The preferred anionic co-surfactants of the invention in combination with the other components of the composition provide

excellent cleaning and outstanding performance from the standpoints of residual spotting and filming. However, many of these co-surfactants may also be high sudsing thereby requiring the addition of LFNI, LFNI in combination with alternate suds suppressors as further disclosed hereinafter, or alternate suds suppressors without conventional LFNI components.

Long-Chain Amine Oxide Solubilizing Aids

Although short-chain amine oxides do not provide the cleaning effect of the essential long-chain amine oxide component of the invention, it has been discovered that adding short-chain amine oxides, such as octyldimethylamine oxide, decyldimethylamine oxide, dodecylamine oxide and tetradecylamine oxide as solubilizing aids to the long-chain amine oxide can be desirable. This is especially preferred if the composition is for use in cold-fill automatic dishwashing appliances. When present, a short-chain amine oxide solubilizer is preferably at not more than 1/10 of the total mass of the cleaning amine oxide component. Thus, levels of short-chain amine oxide are typically in the range from about 0 to about 2.0%, preferably about 0.1% to about 1% of the ADD composition. Moreover, it has been discovered that a short-chain amine oxide, if used, is preferably uniformly dispersed within the long-chain amine oxide rather than being added to the ADD in a separate particle.

When the granular automatic dishwashing compositions are destined for use in hot-fill automatic dishwashing appliances, e.g., those commonly available in the United States, the essential long-chain amine oxide preferably comprises $R^1=C_{18}$ and is preferred over $R^1=C_{16}$ on grounds of mass efficiency; in this circumstance the use of short-chain amine oxide solubilizers is typically avoided.

Non-amine oxide solubilizing aids can be substituted, for example, solid-form alcohols or alcohol ethoxylates (the same as may be independently used for sheeting action or protection of the long-chain amine oxide from water discussed hereinabove) can be used for this purpose.

Silicone and Phosphate Ester Suds Suppressors

The ADDs of the invention can optionally contain an alkyl phosphate ester suds suppressor, a silicone suds suppressor, or combinations thereof. Levels in general are from 0% to about 10%, preferably, from about 0.001% to about 5%. Typical levels tend to be low, e.g., from about 0.01% to about 3% when a silicone suds suppressor is used. Preferred non-phosphate compositions omit the phosphate ester component entirely.

Silicone suds suppressor technology and other defoaming agents useful herein are extensively documented in "Defoaming, Theory and Industrial Applications", Ed., P.R. Garrett, Marcel Dekker, N.Y., 1973, ISBN 0-8247-8770-6, incorporated herein by reference. See especially the chapters entitled "Foam control in Detergent Products" (Ferch et al) and "Surfactant Antifoams" (Blease et al). See also U.S. Patents 3,933,672 and 4,136,045. Highly preferred silicone suds suppressors are the compounded types known for use in laundry detergents such as heavy-duty granules, although types hitherto used only in heavy-duty liquid detergents may also be incorporated in the instant compositions. For example, polydimethylsiloxanes having trimethylsilyl or alternate endblocking units may be used as the silicone. These may be compounded with silica and/or with surface-active nonsilicon components, as illustrated by a suds suppressor comprising 12% silicone/ silica, 18% stearyl alcohol and 70% starch in granular form. A suitable commercial source of the silicone active compounds is Dow Corning Corp.

Levels of the suds suppressor depend to some extent on the sudsing tendency of the composition, for example, an ADD for use at 2000 ppm comprising 2% octadecyldimethylamine oxide may not require the presence of a suds suppressor. Indeed, it is an advantage of the present invention to select cleaning-effective amine oxides which are inherently much lower in foam-forming tendencies than the typical coco amine oxides. In contrast, formulations in which amine oxide is combined with a high-foaming anionic cosurfactant, e.g., alkyl ethoxy sulfate, benefit greatly from the presence of component (f).

Phosphate esters have also been asserted to provide some protection of silver and silver-plated utensil surfaces, however, the instant compositions can have excellent silvercare without a phosphate ester component. Without being limited by theory, it is believed that lower pH formulations, e.g., those having pH of 9.5 and below, plus the presence of the essential amine oxide, both contribute to improved silver care.

If it is desired nonetheless to use a phosphate ester, suitable compounds are disclosed in U.S. Patent 3,314,891, issued April 18, 1967, to Schmolka et al, incorporated herein by reference. Preferred alkyl phosphate esters contain from 16-20 carbon atoms. Highly preferred alkyl phosphate esters are monostearyl acid phosphate or monooleyl acid phosphate, or salts thereof, particularly alkali metal salts, or mixtures thereof.

It has been found preferable to avoid the use of simple calcium-precipitating soaps as antifoams in the present compositions as they tend to deposit on the dishware. Indeed, phosphate esters are not entirely free of such problems and the formulator will generally choose to minimize the content of potentially depositing antifoams in the instant compositions.

Detergent Enzymes (including enzyme adjuncts)

The compositions of this invention may optionally, but preferably, contain from 0 to about 8%, preferably from about 0.001% to about 5%, more preferably from about 0.003% to about 4%, most preferably from about 0.005% to about 3%, by weight, of active detergent enzyme. The knowledgeable formulator will appreciate that different enzymes should be selected depending on the pH range of the ADD composition. Thus, Savinase® may be preferred in the instant compositions when formulated to deliver wash pH of 10, whereas Alcalase® may be preferred when the ADDs deliver wash pH of, say, 8 to 9. Moreover, the formulator will generally select enzyme variants with enhanced bleach compatibility when formulating oxygen bleaches containing compositions of the present invention.

In general, the preferred detergent enzyme herein is selected from the group consisting of proteases, amylases, lipases and

mixtures thereof. Most preferred are proteases or amylases or mixtures thereof.

The proteolytic enzyme can be of animal, vegetable or microorganism (preferred) origin. More preferred is serine proteolytic enzyme of bacterial origin. Purified or nonpurified forms of enzyme may be used. Proteolytic enzymes produced by chemically or genetically modified mutants are included by definition, as are close structural enzyme variants. Particularly preferred by way of proteolytic enzyme is bacterial serine proteolytic enzyme obtained from *Bacillus*, *Bacillus subtilis* and/or *Bacillus licheniformis*. Suitable commercial proteolytic enzymes include Alcalase®, Esperase®, Durazym®, Savinase®, Maxatase®, Maxacal®, and Maxapem® 15 (protein engineered Maxacal); Purafect® and subtilisin BPN and BPN' are also commercially available. Preferred proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine proteolytic enzyme which is called "Protease A" herein. Some preferred proteolytic enzymes, especially in the more alkaline ADDs herein, e.g., those delivering wash pH in the range from about 9 to about 10.5, are selected from the group consisting of Savinase®, Esperase®, Maxacal®, Purafect®, BPN', Protease A and Protease B, and mixtures thereof. Savinase® is most preferred.

Preferred lipase-containing compositions comprise from about 0.001 to about 0.01% lipase, from about 2% to about 5% amine oxide and from about 1% to about 3% low foaming nonionic surfactant.

Suitable lipases for use herein include those of bacterial, animal, and fungal origin, including those from chemically or genetically modified mutants. Suitable bacterial lipases include those produced by *Pseudomonas*, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034, incorporated herein by reference. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase produced from the microorganism *Pseudomonas fluorescens* IAM

1057. This lipase and a method for its purification have been described in Japanese Patent Application 53-20487, laid open on February 24, 1978, which is incorporated herein by reference. This lipase is available under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Such lipases should show a positive immunological cross reaction with the Amano-P antibody, using the standard and well-known immunodiffusion procedure according to Oucheterlon (Acta. Med. Scan., 133, pages 76-79 (1950)). These lipases, and a method for their immunological cross-reaction with Amano-P, are also described in U.S. Patent 4,707,291, Thom et al., issued November 17, 1987, incorporated herein by reference. Typical examples thereof are the Amano-P lipase, the lipase ex *Pseudomonas fragi* FERM P 1339 (available under the trade name Amano-B), lipase ex *Pseudomonas nitroreducens* var. *lipolyticum* FERM P 1338 (available under the trade name Amano-CES), lipases ex *Chromobacter viscosum* var. *lipolyticum* NRRLb 3673, and further *Chromobacter viscosum* lipases, and lipases ex *Pseudomonas gladioli*. A preferred lipase is derived from *Pseudomonas pseudoalcaligenes*, which is described in Granted European Patent, EP-B-0218272. Other lipases of interest are Amano AKG and Bacillis Sp lipase (e.g. Solvay enzymes). Additional lipases which are of interest where they are compatible with the composition are those described in EP A 0 339 681, published November 28, 1990, EP A 0 385 401, published September 5, 1990, EO A Q 218 272, published April 15, 1987, and PCT/DK 88/00177, published May 18, 1989, all incorporated herein by reference.

Suitable fungal lipases include those produced by *Humicola lanuginosa* and *Thermomyces lanuginosus*. Most preferred is lipase obtained by cloning the gene from *Humicola lanuginosa* and expressing the gene in *Aspergillus oryzae* as described in European Patent Application 0 258 068, incorporated herein by reference, commercially available under the trade name Lipolase® from Novo-Nordisk.

Any amylase suitable for use in a dishwashing detergent composition can be used in these compositions. Amylases include for example, α -amylases obtained from a special strain of B.

licheniforms, described in more detail in British Patent Specification No. 1,296,839. Amylolytic enzymes include, for example, RapidaseTM, MaxamylTM, TermamylTM and BANTM. In a preferred embodiment, from about 0.001% to about 5%, preferably 5 0.005% to about 3%, by weight of active amylase can be used. Preferably from about 0.005% to about 3% by weight of active protease can be used. Preferably the amylase is MaxamylTM and/or TermamylTM and the protease is Savinase[®] and/or protease B. As in the case of proteases, the formulator will use ordinary skill in 10 selecting amylases or lipases which exhibit good activity within the pH range of the ADD composition.

Enzyme Stabilizing System

Preferred enzyme-containing compositions herein may comprise from about 0.001% to about 10%, preferably from about 0.005% to 15 about 8%, most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the deterative enzyme. Such stabilizing systems can comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acid, 20 boronic acid, and mixtures thereof.

The stabilizing system of the ADDs herein may further comprise from 0 to about 10%, preferably from about 0.01% to about 6% by weight, of chlorine bleach scavengers, added to prevent 25 chlorine bleach species present in many water supplies from attacking and inactivating the enzymes, especially under alkaline conditions. While chlorine levels in water may be small, typically in the range from about 0.5 ppm to about 1.75 ppm, the available chlorine in the total volume of water that comes in contact with the enzyme during dishwashing is usually large; 30 accordingly, enzyme stability in-use can be problematic.

Suitable chlorine scavenger anions are widely available, indeed ubiquitous, and are illustrated by salts containing ammonium cations or sulfite, bisulfite, thiosulfite, thiosulfate, iodide, etc. Antioxidants such as carbamate, ascorbate, etc., 35 organic amines such as ethylenediaminetetracetic acid (EDTA) or alkali metal salt thereof, monoethanolamine (MEA), and mixtures thereof can likewise be used. Other conventional scavengers such

as bisulfate, nitrate, chloride, sources of hydrogen peroxide such as sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate, as well as phosphate, condensed phosphate, acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc. and mixtures thereof can be used if desired. In general, since the chlorine scavenger function can be performed by several of the ingredients separately listed under better recognized functions, (e.g., other components of the invention including oxygen bleaches), there is no requirement to add a separate chlorine scavenger unless a compound performing that function to the desired extent is absent from an enzyme-containing embodiment of the invention; even then, the scavenger is added only for optimum results. Moreover, the formulator will exercise a chemist's normal skill in avoiding the use of any scavenger which is majorly incompatible with other optional ingredients, if used. For example, formulation chemists generally recognize that combinations of reducing agents such as thiosulfate with strong oxidizers such as percarbonate are not wisely made unless the reducing agent is protected from the oxidizing agent in the solid-form ADD composition. In relation to the use of ammonium salts, such salts can be simply admixed with the detergent composition but are prone to adsorb water and/or liberate ammonia during storage. Accordingly, such materials, if present, are desirably protected in a particle such as that described in U.S. Patent 4,652,392, Baginski et al.

Dispersant Polymer

Preferred compositions herein may additionally contain a dispersant polymer. When present, a dispersant polymer in the instant ADD compositions is typically in the range from 0 to about 25%, preferably from about 0.5% to about 20%, more preferably from about 1% to about 7% by weight of the ADD composition. Dispersant polymers are useful for improved filming performance of the present ADD compositions, especially in higher pH embodiments, such as those in which wash pH exceeds about 9.5. Particularly preferred are polymers which inhibit the deposition of calcium carbonate or magnesium silicate on dishware.

Dispersant polymers suitable for use herein are illustrated by the film-forming polymers described in U.S. Pat. No. 4,379,080 (Murphy), issued Apr. 5, 1983, incorporated herein by reference.

5 Suitable polymers are preferably at least partially neutralized or alkali metal, ammonium or substituted ammonium (e.g., mono-, di- or triethanolammonium) salts of polycarboxylic acids. The alkali metal, especially sodium salts are most preferred. While the molecular weight of the polymer can vary over a wide range, it preferably is from about 1000 to about 10 500,000, more preferably is from about 1000 to about 250,000, and most preferably, especially if the ADD is for use in North American automatic dishwashing appliances, is from about 1000 to about 5,000.

15 Other suitable dispersant polymers include those disclosed in U.S. Patent No. 3,308,067 issued March 7, 1967, to Diehl, incorporated herein by reference. Unsaturated monomeric acids that can be polymerized to form suitable dispersant polymers include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalononic acid. The presence of monomeric 20 segments containing no carboxylate radicals such as methyl vinyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 50% by weight of the dispersant polymer.

25 Copolymers of acrylamide and acrylate having a molecular weight of from about 3,000 to about 100,000, preferably from about 4,000 to about 20,000, and an acrylamide content of less than about 50%, preferably less than about 20%, by weight of the dispersant polymer can also be used. Most preferably, such dispersant polymer has a molecular weight of from about 4,000 to 30 about 20,000 and an acrylamide content of from about 0% to about 15%, by weight of the polymer.

35 Particularly preferred dispersant polymers are low molecular weight modified polyacrylate copolymers. Such copolymers contain as monomer units: a) from about 90% to about 10%, preferably from about 80% to about 20% by weight acrylic acid or its salts and b) from about 10% to about 90%, preferably from about 20% to about

80% by weight of a substituted acrylic monomer or its salt and have the general formula: $-\left[\left(\text{C}(\text{R}^2)\text{C}(\text{R}^1)\text{C}(\text{O})\text{OR}^3\right)\right]-$ wherein the incomplete valencies inside the square braces are hydrogen and at least one of the substituents R^1 , R^2 or R^3 , preferably R^1 or R^2 , is a 1 to 4 carbon alkyl or hydroxyalkyl group, R^1 or R^2 can be a hydrogen and R^3 can be a hydrogen or alkali metal salt. Most preferred is a substituted acrylic monomer wherein R^1 is methyl, R^2 is hydrogen and R^3 is sodium.

The low molecular weight polyacrylate dispersant polymer preferably has a molecular weight of less than about 15,000, preferably from about 500 to about 10,000, most preferably from about 1,000 to about 5,000. The most preferred polyacrylate copolymer for use herein has a molecular weight of 3500 and is the fully neutralized form of the polymer comprising about 70% by weight acrylic acid and about 30% by weight methacrylic acid.

Other suitable modified polyacrylate copolymers include the low molecular weight copolymers of unsaturated aliphatic carboxylic acids disclosed in U.S. Patents 4,530,766, and 5,084,535, both incorporated herein by reference.

Agglomerated forms of the present invention may employ aqueous solutions of polymer dispersants as liquid binders for making the agglomerate (particularly when the composition consists of a mixture of sodium citrate and sodium carbonate). Especially preferred are polyacrylates with an average molecular weight of from about 1,000 to about 10,000, and acrylate/maleate or acrylate/ fumarate copolymers with an average molecular weight of from about 2,000 to about 80,000 and a ratio of acrylate to maleate or fumarate segments of from about 30:1 to about 1:2. Examples of such copolymers based on a mixture of unsaturated mono- and dicarboxylate monomers are disclosed in European Patent Application No. 66,915, published December 15, 1982, incorporated herein by reference.

Other, less preferred dispersant polymers useful herein include the polyethylene glycols and polypropylene glycols having a molecular weight of from about 950 to about 30,000 which can be obtained from the Dow Chemical Company of Midland, Michigan. Such compounds for example, having a melting point within the range of

from about 30° to about 100°C can be obtained at molecular weights of 1450, 3400, 4500, 6000, 7400, 9500, and 20,000. Such compounds are formed by the polymerization of ethylene glycol or propylene glycol with the requisite number of moles of ethylene or propylene oxide to provide the desired molecular weight and melting point of the respective polyethylene glycol and polypropylene glycol. The polyethylene, polypropylene and mixed glycols are referred to using the formula $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_m(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_n(\text{CH}(\text{CH}_3)\text{CH}_2\text{O})\text{OH}$ wherein m, n, and o are integers satisfying the molecular weight and temperature requirements given above.

Yet other dispersant polymers not preferred but useful herein include the cellulose sulfate esters such as cellulose acetate sulfate, cellulose sulfate, hydroxyethyl cellulose sulfate, methylcellulose sulfate, and hydroxypropylcellulose sulfate. Sodium cellulose sulfate is the most preferred polymer of this group.

Other suitable dispersant polymers, again not as preferred as the above-identified acrylate and acrylate/maleate polymers, are the carboxylated polysaccharides, particularly starches, celluloses and alginates, described in U.S. Pat. No. 3,723,322, Diehl, issued Mar. 27, 1973; the dextrin esters of polycarboxylic acids disclosed in U.S. Pat. No. 3,929,107, Thompson, issued Nov. 11, 1975; the hydroxyalkyl starch ethers, starch esters, oxidized starches, dextrans and starch hydrolysates described in U.S. Pat. No. 3,803,285, Jensen, issued Apr. 9, 1974; the carboxylated starches described in U.S. Pat. No. 3,629,121, Eldib, issued Dec. 21, 1971; and the dextrin starches described in U.S. Pat. No. 4,141,841, McDonald, issued Feb. 27, 1979; all incorporated herein by reference. Preferred cellulose-derived dispersant polymers are the carboxymethyl celluloses.

Bleach

The ADD compositions of the present invention optionally contain an amount of bleach sufficient to provide from 0% to about 5%, preferably from about 0.1% to about 5.0%, most preferably from about 0.5% to about 3.0%, of available chlorine (as Cl₂) or available oxygen (as O) by weight of the ADD.

An inorganic chlorine bleach ingredient such as chlorinated trisodium phosphate can be utilized, but organic chlorine bleaches such as the chlorocyanurates are preferred. Water-soluble dichlorocyanurates such as sodium or potassium dichloroisocyanurate dihydrate are particularly preferred.

Available chlorine or available oxygen of an ADD or a bleach component is the equivalent bleaching chlorine content thereof expressed as % equivalent Cl₂ by weight or the bleaching oxygen content thereof expressed as %O. For example, commercially available sodium perborate monohydrate typically has an available oxygen content for bleaching purposes of about 15% (theory predicts a maximum of about 16%). Conventional analytical methods for determining available chlorine comprise addition of an excess of an iodide salt and titration of the liberated free iodine with a reducing agent such as thiosulfate. Methods for determining available oxygen of a formula after manufacture share similar chemical principles but depend on whether the oxygen bleach incorporated therein is a simple hydrogen peroxide source such as sodium perborate or percarbonate, is an activated type (e.g., perborate with tetra-acetyl ethylenediamine) or comprises a preformed peracid such as monoperphthalic acid. Analysis of peroxygen compounds is well-known in the art: see, for example, the publications of Swern, such as "Organic Peroxides", Vol. I, D.H. Swern, Editor; Wiley, New York, 1970, LC # 72-84965, incorporated by reference. See for example the calculation of "percent active oxygen" at page 499. This term is equivalent to the terms "available oxygen" or "percent available oxygen" as used herein.

As noted the ADD compositions manufactured according to the present invention can contain bleach components other than the chlorine type. For example, oxygen-type bleaches described in U.S. Pat. No. 4,412,934 (Chung et al), issued Nov. 1, 1983, and peroxyacid bleaches described in European Patent Application 033,2259, Sagel et al, published Sept. 13, 1989, both incorporated herein by reference, can be used as a partial or complete replacement of chlorine bleach. Oxygen bleaches are particularly

preferred when it is desirable to reduce the total chlorine content or use enzyme in the instant compositions.

Preferred oxygen bleaches herein are sodium perborate monohydrate and sodium percarbonate, optionally combined with conventional activators. ADDs with optimum bleaching action are typically higher-pH embodiments (wash pH 9.5 or higher) of the invention. For excellent results at lower pH's (e.g., 9 and below), it is desirable to formulate perborate or percarbonate with benzoyloxybenzenesulfonate activator (or equivalent operating well at low pH), or to use a preformed peracid, such as m-chloroperbenzoic acid or potassium monopersulfate, or a chlorine bleach. In the latter instances there is evidently no need to react hydroxgen peroxide (or HOO-) with activator, hence optimum bleaching can be secured without first having to drive peracid formation. When such active bleaching compounds are used in the presence of deterative enzymes, it is highly preferred to delay the onset of bleaching action, e.g., by coating the bleach with a slow-dissolving nonionic surfactant, so that the enzyme has adequate opportunity to carry out its cleaning function before the bleach is delivered to the wash. Coatings may include LFNI coating agents, and may in general be applied to any of (i) activator (ii) peracid and (iii) pH-adjusting agents.

Other Optional Adjuncts

Depending on whether a greater or lesser degree of compactness is required, filler materials can also be present in the instant ADDs. These include sucrose, sucrose esters, sodium chloride, sodium sulfate, potassium chloride, potassium sulfate, etc., in amounts up to about 70%, preferably from 0% to about 40% of the ADD composition. Preferred filler is sodium sulfate, especially in good grades having at most low levels of trace impurities.

Sodium sulfate used herein preferably has a purity sufficient to ensure it is non-reactive with bleach; it may also be treated with low levels of sequestrants, such as phosphonates in magnesium-salt form. Note that preferences, in terms of purity sufficient to avoid decomposing bleach, applies also to component (b) ingredients.

Hydrotrope materials such as sodium benzene sulfonate, sodium toluene sulfonate, sodium cumene sulfonate, etc., can be present in minor amounts.

5 Bleach-stable perfumes (stable as to odor); and bleach-stable dyes (such as those disclosed in U.S. Patent 4,714,562, Roselle et al, issued December 22, 1987); can also be added to the present compositions in appropriate amounts. Other common detergent ingredients are not excluded.

10 Since certain ADD compositions herein can contain water-sensitive ingredients, e.g., in embodiments comprising anhydrous amine oxides or anhydrous citric acid, it is desirable to keep the free moisture content of the ADDs at a minimum, e.g., 7% or less, preferably 4% or less of the ADD; and to provide packaging which is substantially impermeable to water and carbon dioxide. Plastic bottles, including refillable or recyclable, 15 types, as well as conventional barrier cartons or boxes are, generally suitable. When ingredients are not highly compatible, e.g., mixtures of silicates and citric acid, it may further be desirable to coat at least one such ingredient with a low-foaming nonionic surfactant for protection. There are numerous waxy 20 materials which can readily be used to form suitable coated particles of any such otherwise incompatible components.

25 Further, in connection with combining the essential components of the present invention and other ADD-useful ingredients herein, the preferred manufacturing process generally avoids exposing the amine oxide to excessively high temperatures. Preferred manufacturing temperatures for any step or steps involving the amine oxide can generally be identified by checking amine oxide in the final ADD product for impurity or decomposition product. See Kirk-Othmer, Encyclopedia of Chemical Technology, 30 "Amine Oxides", for additional information regarding Amine Oxide thermal stability. Several preferred embodiments herein are readily prepared by admixing amine oxides at ambient temperature or, less preferably, by admixing amine oxides to the otherwise finished ADD at temperatures up to about 65°C. 35

The following examples illustrate the compositions of the present invention. All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified.

Method for Cleaning

5 The present invention also encompasses a method for cleaning soiled tableware comprising contacting said tableware with an aqueous medium having a pH in the range from about 6 to about 11, more preferably from about 8 to about 10, and comprising at least about 1 ppm (part per million by weight) of an amine oxide having
10 one long-chain and two short-chains (in accordance with the above formula I definition); said aqueous medium being formed by dissolving a solid-form automatic dishwashing detergent containing the essential amine oxide component in an automatic dishwashing machine.

15

EXAMPLE I

Granular automatic dishwashing detergents of the present invention are as follows:

Table 1

| | | <u>% by weight</u> | | | |
|----|---|--------------------|----------|----------|----------|
| | | <u>A</u> | <u>B</u> | <u>C</u> | <u>D</u> |
| 20 | <u>Ingredients</u> | | | | |
| | Octadecyldimethylamine-N-oxide dihydrate ¹ | - | 2.00 | 2.00 | - |
| | Hexadecyldimethylamine-N-oxide dihydrate ² | - | - | - | - |
| 25 | DMAO Blend ³ | - | - | - | 5.00 |
| | Octadecyldimethylamine-N-oxide, anhydrous | 2.00 | - | - | - |
| | Sodium citrate, dihydrate | 19.00 | 19.00 | 19.00 | 19.00 |
| 30 | Sodium carbonate or bicarbonate | 9.50 | 9.50 | 9.50 | 10.00 |
| | Hydrated 2.0 ratio sodium silicate | 8.50 | 8.50 | 8.50 | 8.50 |
| | 3500MW modified polyacrylate (active basis) | 6.00 | 6.00 | 6.00 | 6.00 |
| | C12-15 alcohol triethoxysulfate ⁴ | - | 0.05 | - | - |
| 35 | Nonionic surfactant ⁵ | 2.00 | 2.00 | - | 2.00 |
| | Sodium percarbonate | 11.40 | 11.40 | 11.40 | 11.40 |

| | | | | | |
|----|--|-------------------|------|------|------|
| | Tetra-acetylatedethylenediamine (92% active) | 3.80 | 3.80 | 3.80 | 3.80 |
| | S,S-ethylenediaminedisuccinic acid, magnesium salt | - | 0.10 | - | 0.10 |
| 5 | Ethylenediamine penta(methylenephosphonic) acid, magnesium salt | - | - | - | - |
| | Alcalase® 3T | 2.40 | 2.40 | 2.40 | 2.40 |
| | Rapidase® | - | - | - | 1.0 |
| | Termamyl® 60T | 1.10 | 1.10 | 1.10 | 1.10 |
| 10 | Lipase ⁶ | - | - | - | 0.01 |
| | Suds suppressor | - | 4.00 | - | 4.00 |
| | Perfume, dye, water and filler | -----balance----- | | | |

1 C₁₈DMAO.2H₂O ADMOX 18, Ethyl Corp.

15 2 C₁₈DMAO.2H₂O ADMOX 16, Ethyl Corp.

3 80:20 wt. blend of C₁₈DMAO2H₂O/C₁₆DMAO2H₂O

4 Neodol 12/15 E3S, Shell Corp.

5 SLF 18, Olin Corp.

6 From psuedomonas psuedoalcaligenes, 100,000 LU/g

20

| | | <u>% by weight</u> | | |
|--------------------|--|--------------------|----------|----------|
| <u>Ingredients</u> | | <u>E</u> | <u>F</u> | <u>G</u> |
| 25 | Octadecyldimethylamine-N-oxide dihydrate ¹ | - | 2.00 | - |
| | Hexadecyldimethylamine-N-oxide dihydrate ² | - | - | - |
| | DMAO Blend ³ | 5.00 | - | 5.00 |
| 30 | Octadecyldimethylamine-N-oxide, anhydrous | - | - | - |
| | Sodium citrate, dihydrate | 19.00 | 15.00 | 20.00 |
| | Sodium carbonate or bicarbonate | 9.00 | 10.00 | 10.00 |
| | Hydrated 2.0 ratio sodium silicate | 8.50 | 7.00 | 9.00 |
| | 3500MW modified polyacrylate (active basis) | 6.00 | - | - |
| 35 | C ₁₂₋₁₅ alcohol triethoxysulfate ⁴ | 5.00 | - | - |
| | Nonionic surfactant ⁵ | 2.00 | 1.00 | - |
| | Sodium percarbonate | 11.40 | 12.00 | 12.00 |

| | | | | |
|----|---|-------------------|------|------|
| | Tetra-acetylated ethylenediamine | | | |
| | (92% active) | - | - | - |
| | S,S-ethylenediamine disuccinic acid, | | | |
| | magnesium salt | - | - | - |
| 5 | Ethylenediamine penta(methylenephosphonic | | | |
| | acid, magnesium salt | - | 0.10 | 0.10 |
| | Alcalase® 3T | 2.40 | 2.0 | - |
| | Rapidase® | - | 1.0 | - |
| | Termamyl® 60T | 1.10 | - | - |
| 10 | Lipase ⁶ | 0.10 | - | - |
| | Suds suppressor | 4.00 | - | - |
| | Perfume, dye, water and filler | -----balance----- | | |

1 C₁₈DMAO.2H₂O ADMOX 18, Ethyl Corp.

15 2 C₁₈DMAO.2H₂O ADMOX 16, Ethyl Corp.

3 80:20 wt. blend of C₁₈DMAO2H₂O/C₁₆DMAO2H₂O

4 Neodol 12/15 E3S, Shell Corp.

5 SLF 18, Olin Corp.

6 From psuedomonas psuedoalcaligenes, 100,000 LU/g

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The compositions are used at a concentration of about 0.28% in North American GE Potscrubber dishwashers; or at a concentration of about 0.4% in European Miele dishwashers, to remove lipstick from white polystyrene cups. Prior to washing, the lipstick is in the form of a thin, uniform film covering about 1/2" by 2" of the outer surface of each cup. A lipstick used for testing is "Cover Girl" Remarkable, "Raspberry Rage". It is applied directly, then smoothed out and excess removed using a cotton tip, prior to washing in the dishwasher. The compositions produce excellent removal. Otherwise identical compositions lacking the amine oxide remove lipstick less efficiently and/or produce more film on clear polystyrene tumblers included in the wash.

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EXAMPLE II

Granular automatic dishwashing detergents of the present invention are—as follows:

Table 2

| | <u>Ingredients</u> | <u>% by weight</u> | | |
|----|------------------------------------|--------------------|----------|----------|
| | | <u>H</u> | <u>I</u> | <u>J</u> |
| | Octadecyldimethylamine-N-oxide | | | |
| 5 | dihydrate ¹ | 2.00 | - | - |
| | Sodium citrate, dihydrate | 19.00 | 19.00 | 19.00 |
| | Sodium carbonate or bicarbonate | 20.00 | 20.00 | 20.00 |
| | Hydrated 2.0 ratio sodium silicate | 19.00 | 19.00 | 19.00 |
| | 3500MW modified polyacrylate | 6.00 | 6.00 | 6.00 |
| 10 | (active basis) | | | |
| | Sodium sulfate anhydrous | 23.00 | 23.00 | 23.00 |
| | Nonionic surfactant ² | 2.00 | 2.00 | - |
| | Sodium percarbonate | 11.40 | 11.40 | 11.40 |
| | Tetra-acetylatedethylenediamine | | | |
| 15 | (92% active) | - | - | - |
| | Savinase® 6.0% | 2.40 | 2.40 | 2.40 |
| | Termamyl® 60T | 1.10 | 1.10 | 1.10 |
| | Lipase ³ | - | - | - |
| | Suds suppressor | - | 4.0 | - |
| 20 | Perfume, dye, water and filler | -----balance----- | | |

¹(C₁₈DMAO.2H₂) ADMOX 18, Ethyl Corp.

² SLF 18, Olin Corp.

³ From pseudomonas pseudoalcaligenes, 100,000 LU/g

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EXAMPLE III

Granular automatic dishwashing detergents of the present invention are as follows:

Table 3

| | <u>Ingredients</u> | <u>% by weight</u> | | |
|----|--------------------------------|--------------------|----------|----------|
| | | <u>K</u> | <u>L</u> | <u>M</u> |
| 30 | Octadecyldimethylamine-N-oxide | | | |
| | dihydrate ¹ | 2.00 | - | - |
| | Hexadecyldimethylamine-N-oxide | | | |
| 35 | dihydrate ² | - | 5.00 | - |
| | BHEAO Blend ³ | - | - | 5.00 |
| | Sodium citrate, dihydrate | 37.00 | 29.00 | 29.00 |

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| | | | | |
|----|--|-------------------|-------|-------|
| | Hydrated 2.0 ratio sodium silicate | 28.00 | 26.00 | 26.00 |
| | Dispersant polymer ⁴ (92% active) | 4.00 | 4.00 | 4.00 |
| | Nonionic surfactant ⁵ | 1.50 | 1.50 | 1.50 |
| | Sodium perborate (as AvO) | 1.50 | 0.80 | 0.80 |
| 5 | Tetra-acetylated ethylenediamine (92% active) | 3.00 | 4.00 | 4.00 |
| | Savinase® 6.0T | 2.20 | 2.20 | 2.00 |
| | Termamyl® 60T | 1.50 | 1.10 | 1.10 |
| | Lipase ⁵ | - | - | 0.10 |
| 10 | Benzotriazole | 0.20 | 0.20 | - |
| | Paraffin | 0.50 | - | 0.50 |
| | Perfume, dye, water and filler | -----balance----- | | |

1 C₁₈DMAO.2H₂O ADMOX 18, Ethyl Corp.

15 2 C₁₈DMAO.2H₂O ADMOX 16, Ethyl Corp.

3 70:30 weight C₁₈/C₁₆ blend of octadecyl bis(hydroxethyl)amine
N-oxide, anhydrous and hexadecylbis(hydroxethyl)amine N-oxide,
anhydrous

4 SOKILAN CP5, dry form

20 5 from pseudomonas pseudoalcaligenes, 100,000 LU/g

WHAT IS CLAIMED IS:

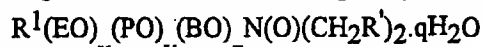
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What is claimed is:

1. A solid-form automatic dishwashing detergent composition comprising from 0.1% to 10% by weight of an amine oxide having the general formula:



5 wherein R^1 represents a saturated or unsaturated hydrocarbyl moiety having a chainlength of from 12 to 24 carbon atoms, x is from 0 to 10, y is from 0 to 10, z is from 0 to 10, R' is H or CH_2OH , q is from 0 to 2, EO represents ethyleneoxy, PO represents propyleneoxy, and BO represents butyleneoxy; provided that when $x+y+z = 0$, R^1 has a chainlength of from 16 to 18 carbon atoms; and further provided that
10 when $x+y+z$ is different from 0, $x+y+z$ has a maximum value of 10; said composition having a pH from 6 to 11.

2. A composition according to Claim 1 wherein R^1 is a primary alkyl moiety and said amine oxide is selected from the group consisting of

- (i) amine oxides according to said general formula wherein $x+y+z$ is 0, the R^1 chainlength is from 16 to 18, $R' = H$ and q is from 0 to 2, preferably $q=2$;
- 5 (ii) amine oxides according to said general formula wherein $x+y+z = 0$, the R^1 chainlength is from 16 to 18, $R' = CH_2OH$ and q is 0;
- (iii) amine oxides according to said general formula wherein $x+y+z = 1$ to 10, the R^1 chainlength is from 12 to 24, $y + z$ is 0, and x is from 1 to 6; and
- (iv) mixtures thereof;
- 10 and wherein said composition is substantially phosphate free.

3. A composition according to any one of the preceding claims comprising from 1% to 7% amine oxide and wherein said amine oxide comprises less than 2% of free amine and 500 ppb of nitrosamine and is substantially free of boron.

4. A composition according to any one of the preceding claims, comprising

- (a) from 1.5% to 5% of said amine oxide; and
- (b) from 1% to 50% of a pH adjusting component selected from the group consisting of water-soluble inorganic salts and water-soluble organic or
5 inorganic nonphosphorus builder salts.

5. A composition according to any one of the preceding claims having a pH between 8 and 11, preferably from 9 to 10.5, wherein said pH adjusting component is a salt or salt/builder mixture selected from
- (i) sodium carbonate or sesquicarbonate
 - 5 (ii) sodium silicate, preferably hydrous sodium silicate having SiO_2 : Na_2O ratio of 2:1;
 - (iii) sodium citrate
 - (iv) citric acid
 - (v) sodium bicarbonate
 - 10 (vi) sodium borate
 - (vii) sodium hydroxide; and
 - (viii) mixtures thereof.
6. A composition according to any one of the preceding claims further comprising from 0.1% to 10% of a low foaming nonionic surfactant other than amine oxide selected from alkoxylated alcohols, glucosamides and mixtures thereof.
7. A composition according to any one of the preceding claims further comprising from 0.1% to 8% of an anionic co-surfactant selected from alkylethoxysulfates, alkylethoxycarboxylates and mixtures thereof.
8. A composition according to any one of the preceding claims further comprising from 0.01% to 1% of a short-chain amine oxide and from 0.001% to 5% of a silicone suds suppressor.
9. A composition according to any one of the preceding claims further comprising from 0.001% to 5% of a detergent enzyme selected from the group consisting of protease, amylase, lipase and mixtures thereof, preferably from 0.005 to 3% by weight protease or amylase.
- 5 10. A composition according to any one of the preceding claims further comprising from 0.5% to 20% of a dispersant polymer selected from polacrylates and polyacrylate copolymers, said polymer having a molecular weight below about 10,000, 0.01% to 6% by weight of an enzyme stabilizing system and sufficient bleach

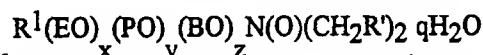
5 to provide from 0.1% to 5.0% by weight of the composition of available oxygen or chlorine.

11. A substantially chlorine-free composition according to any one of the preceding claims wherein said amine oxide is anhydrous.

12. A granular or powdered automatic dishwashing detergent composition which comprises:

- (a) at least 0.2% by weight of a long-chain amine oxide selected from the group consisting of hexadecyldimethylamine N-oxide, octadecyldimethylamine N-oxide, hexadecyldimethylamine N-oxide dihydrate, octadecyldimethylamine N-oxide dihydrate and mixtures thereof;
- 5 (b) from 1% to 50% of a pH adjusting component consisting of water-soluble salt or salt/builder mixture selected from sodium carbonate, sodium sesquicarbonate, sodium silicate, sodium citrate, citric acid, sodium bicarbonate, sodium hydroxide, and mixtures thereof; preferably from 10% to 30% sodium citrate and from 7% to 25% sodium carbonate.
- (c) from 0 to 10% of a low-foaming nonionic surfactant other than amine oxide;
- (d) from 0 to 10% of an anionic cosurfactant;
- (e) from 0 to 2% of a short-chain amine oxide;
- 10 (f) from 0 to 10% of a silicone suds suppressor;
- (g) from 0 to 8% of an active detergent enzyme;
- (h) from 0 to 25% of a dispersant polymer;
- (i) from 0 to 5% of a bleach; and
- 15 (j) from 0 to 40% of sodium sulfate, wherein said composition has a pH of from 8.5 to 10.5, preferably from 9.5 to 10.5.
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13. A method for cleaning soiled tableware comprising contacting said tableware with an aqueous medium comprising at least 1 ppm of an amine oxide having the general formula:



- 5 wherein R^1 represents a saturated or unsaturated hydrocarbyl moiety having a chainlength of from 12 to 24 carbon atoms, x is from 0 to 10, y is from 0 to 10, z is from 0 to 10, R' is H or CH_2OH , q is from 0 to 2, EO represents ethyleneoxy, PO

represents propyleneoxy, and BO represents butyleneoxy; provided that when $x+y+z = 0$, R^1 has a chainlength of from 16 to 18 carbon atoms; and further provided that when $x+y+z$ is different from 0, $x+y+z$ has a maximum value of 10; said composition having a pH from 6 to 11 and formed by dissolving a solid-form automatic dishwashing detergent containing said amine oxide component in an automatic dishwashing machine.

14. A method according to Claim 28 wherein R^1 is a primary alkyl moiety, said amine oxide is selected from the group consisting of
- (i) amine oxides according to said general formula wherein $x+y+z = 0$, the R^1 chainlength is from 16 to 18, $R' = H$ and q is from 0 to 2;
 - 5 (ii) amine oxides according to said general formula wherein $x+y+z = 0$, the R^1 chainlength is from 16 to 18, $R' = CH_2OH$ and $q = 0$;
 - (iii) amine oxides according to said general formula wherein $x+y+z = 1$ to 10, the R^1 chainlength is from 12 to 24, $y + z = 0$, and x is from 1 to 6; and
 - 10 (iv) mixtures of (i)-(iii); wherein said pH is from 8 to 11.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 94/08609

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D1/75 C11D1/825 C11D1/835 C11D1/86 C11D3/386

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| X | DATABASE WPI Section Ch, Week 9139, Derwent Publications Ltd., London, GB; Class A97, AN 91-286183 & JP,A,3 191 000 (KAO CORP) 20 August 1991 see abstract --- | 1-3,6,9, 11,13,14 |
| X | DATABASE WPI Section Ch, Week 9139, Derwent Publications Ltd., London, GB; Class A97, AN 91-286181 & JP,A,3 190 998 (KAO CORP) 20 August 1991 see abstract --- -/-- | 1-3,9, 11,13,14 |

☒ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

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Date of the actual completion of the international search

13 December 1994

Date of mailing of the international search report

21.12.94

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Authorized officer

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 94/08609

| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|--|---|-----------------------|
| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| X | DATABASE WPI Section Ch, Week 8822, Derwent Publications Ltd., London, GB; Class D25, AN 88-151591 & JP,A,63 092 698 (KAO CORP) 23 April 1988 see abstract --- | 1 |
| A | DATABASE WPI Section Ch, Week 8822, Derwent Publications Ltd., London, GB; Class D25, AN 73-65264U & JP,B,48 033 964 (AJINOMOTO CO INC) 23 April 1988 see abstract ----- | 1 |